

# Chapter-20

## Lesson-1

### I – Redox Reactions and Oxidation Numbers (States)

- The **oxidation state** is the charge carried by an atom in an ionic species or the "apparent (pseudo) charge" carried by an atom in molecular species. In any formula, each atom can be assigned a number equal to the atoms oxidation state.
- **Oxidation numbers** make it easier to analyze redox reactions.
- **Oxidation numbers** are assigned to the atoms in a species by the following rules.
  - 1) The sum of the oxidation numbers for every atom in a species must be equal to the total charge of the species.
  - 2) The oxidation number for each atom in a free element is zero.
  - 3) The oxidation number for a monoatomic ion is equal to the charge of the ion.
  - 4) In a compound, the oxidation number for atoms of alkali metals is +1.  
In a compound, the oxidation number for atoms of alkaline earth metals is +2.  
In a compound, the oxidation numbers for atoms of silver, zinc, aluminum, and fluorine are +1, +2, +3, and -1 respectively.
  - 5) In a compound, the oxidation number for atoms of hydrogen is usually +1. In metallic hydrides, the oxidation number for the atoms of hydrogen is -1.
  - 6) In a compound, the oxidation number for oxygen atoms is usually -2. In peroxide, the oxidation number for the two oxygen atoms is -1.
  - 7) In **binary compounds** in which the second element is from Group-15, Group-16, or Group-17, the oxidation numbers are usually -3, -2, and -1 respectively.
  - 8) In most **binary compounds**, the atoms of the first element are assigned a positive oxidation number and the atoms of the second element are assigned a negative oxidation number.

**Q1:** Give the oxidation numbers for the atoms of each element in the following species:

(a) O<sub>2</sub>    (b) H<sub>2</sub>O    (c) H<sub>2</sub>O<sub>2</sub>    (d) OF<sub>2</sub>    (e) FeSO<sub>4</sub>    (f) Hg<sub>2</sub><sup>2+</sup>

**A1:** (a) O = 0

(d) O = +2, F = -1

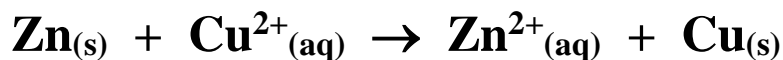
(b) H = +1, O = -2

(e) Fe = +2, S = +6, O = -2

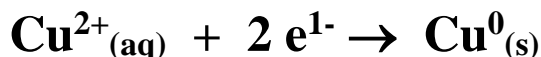
(c) H = +1, O = -1

(f) Hg = +1

- During some chemical reactions there is a transfer of electrons from one species to another.



- These reactions are called reduction-oxidation reactions or redox reactions (for short).
- Reduction occurs when a species gains electrons. (**ger**)



The species that undergoes reduction is said to be reduced.

- When a species gains electrons, it will lose oxidation number. Thus reduction (a gain of electrons) can operationally be defined as a loss in oxidation number.  $\downarrow \text{ox \#} = \uparrow \text{e}^{-}$
- Oxidation occurs when a species loses electrons. (**leo**)

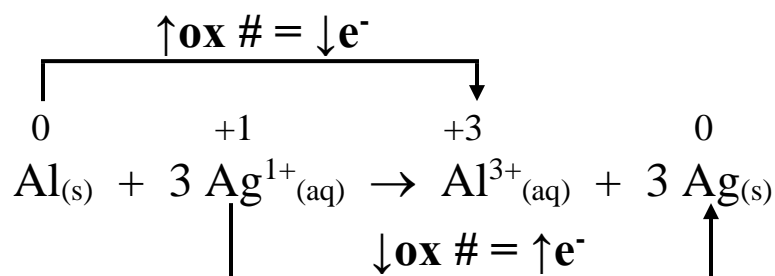


The species that undergoes oxidation is said to be oxidized.

- When a species loses electrons, it will gain oxidation number. Thus oxidation (a loss of electrons) can operationally be defined as a gain in oxidation number.  $\uparrow \text{ox \#} = \downarrow \text{e}^{-}$
- During a redox reaction, the number of electrons lost by the species being oxidized must be equal to the number of electrons being gained by the species being reduced.

**Q2:** For the reaction,  $\text{Al}_{(\text{s})} + 3 \text{Ag}^{1+}_{(\text{aq})} \rightarrow \text{Al}^{3+}_{(\text{aq})} + 3 \text{Ag}_{(\text{s})}$ ,  
 (i) what species is being oxidized?, (ii) what species is being reduced?, and (iii) how many electrons are being transferred?

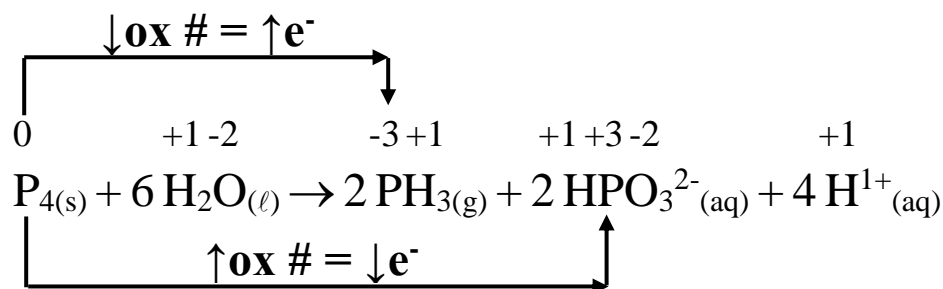
**A2:**



(i)  $\text{Al}_{(\text{s})}$                       (ii)  $\text{Ag}^{1+}_{(\text{aq})}$                       (iii) 3

**Q3:** For the reaction,  $\text{P}_{4(\text{s})} + 6 \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{PH}_{3(\text{g})} + 2 \text{HPO}_3^{2-}_{(\text{aq})} + 4 \text{H}^{1+}_{(\text{aq})}$   
 (i) what species is being oxidized?, (ii) what species is being reduced?, and (iii) how many electrons are being transferred?

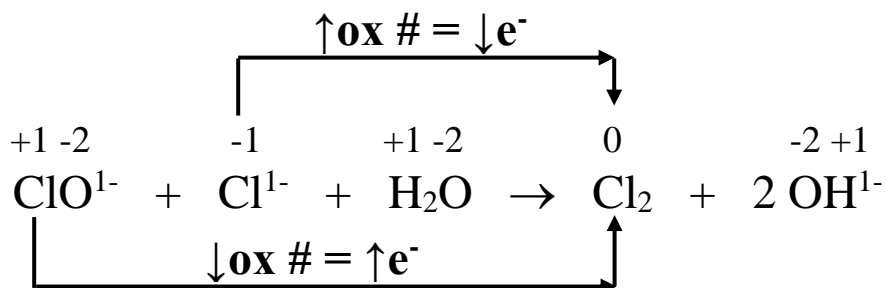
**A3:**



(i)  $\text{P}_{4(\text{s})}$                       (ii)  $\text{P}_{4(\text{s})}$                       (iii) 6

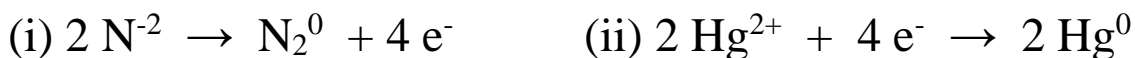
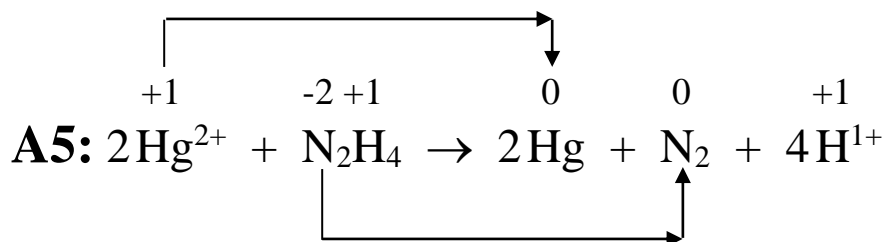
**Q4:** In the following reaction,  $\text{ClO}^{1-} + \text{Cl}^{1-} + \text{H}_2\text{O} \rightarrow \text{Cl}_2 + 2 \text{OH}^{1-}$   
 (i) what species is being oxidized?, (ii) what species is being reduced?, and (iii) how many electrons are being transferred?

**A4:**

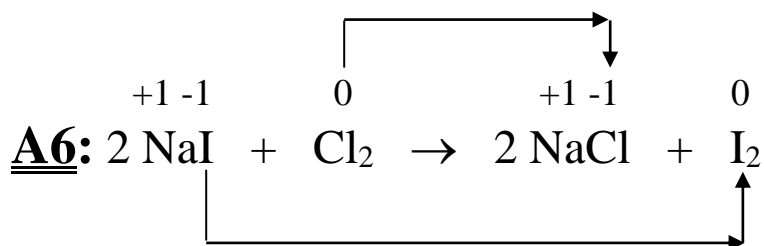


(i) the  $\text{Cl}^{1-}$                       (ii) the  $\text{ClO}^{1-}$                       (iii) 1

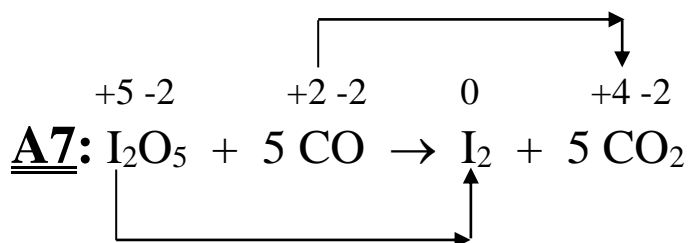
**Q5:** For the following reaction,  $2\text{Hg}^{1+} + \text{N}_2\text{H}_4 \rightarrow 2\text{Hg} + \text{N}_2 + 4\text{H}^{1+}$ ,  
(i) write the oxidation half reaction and (ii) write the reduction half reaction.



**Q6:** For the following reaction,  $2 \text{NaI} + \text{Cl}_2 \rightarrow 2 \text{NaCl} + \text{I}_2$ ,  
(i) write the oxidation half reaction and (ii) write the reduction half reaction.



**Q7:** For the following reaction,  $\text{I}_2\text{O}_5 + 5 \text{CO} \rightarrow \text{I}_2 + 5 \text{CO}_2$ ,  
(i) write the oxidation half reaction and (ii) write the reduction half reaction.



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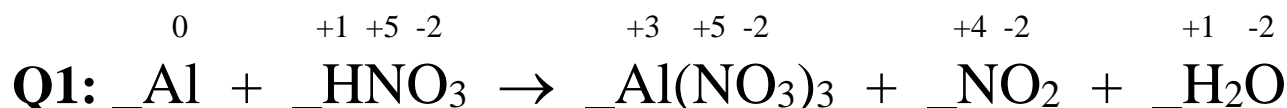
## Lesson-2

### II –Balancing Redox Reactions

#### A) "Simple" Reactions

- The following rules are used to balance redox reactions.
  - 1) Assign oxidation numbers.
  - 2) Write the two half-reactions.
  - 3) Balance the electrons between the half-reactions.
  - 4) Write the net redox reaction.
  - 5) Apply the coefficients for the "unique" species only.
  - 6) Finish balancing the redox equation if necessary.

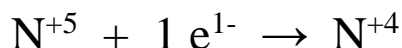
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- 1) **assign the oxidation numbers to each element**



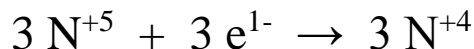
**Write the two half reactions.**



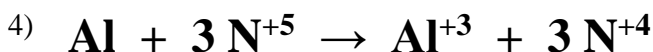
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**Adjust coefficients to balance the electrons**



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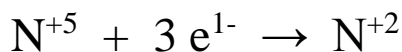
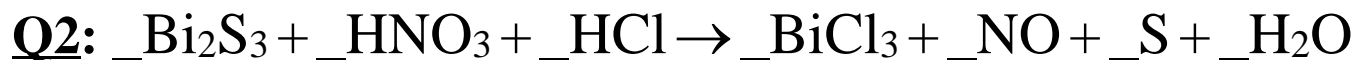
**Only apply coefficients to "unique species".  
N<sup>+5</sup> is NOT a unique species in the reaction.**

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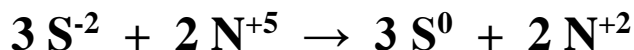


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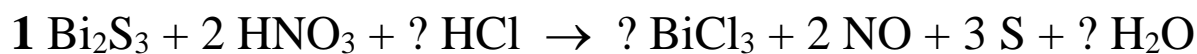




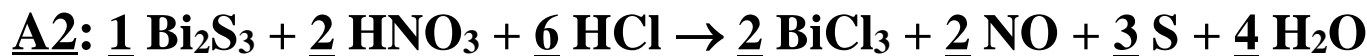
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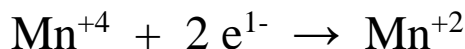
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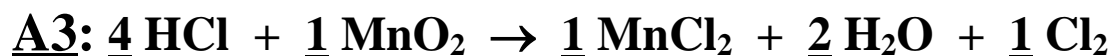
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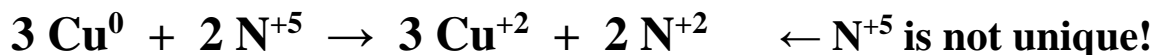


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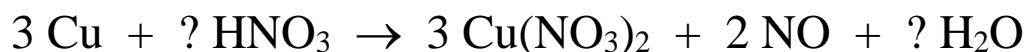




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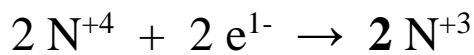
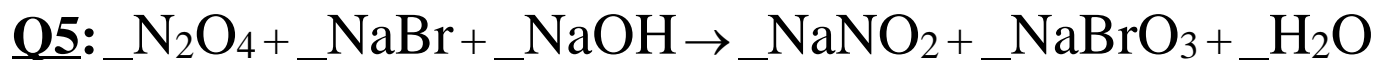
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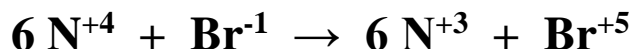
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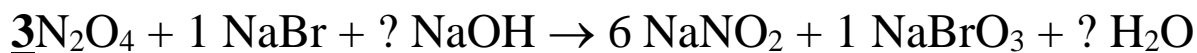
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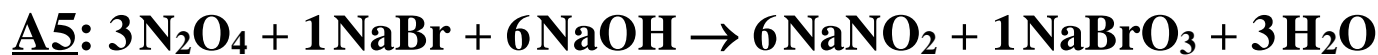
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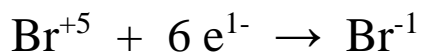
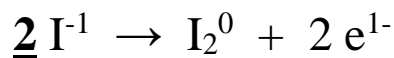
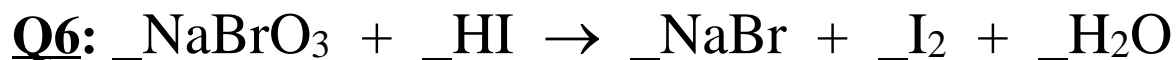


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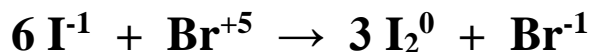


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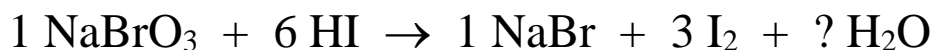




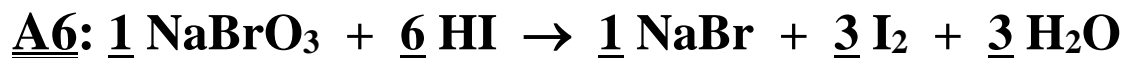
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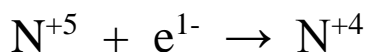
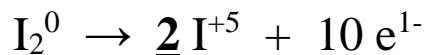
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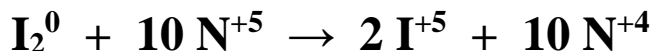
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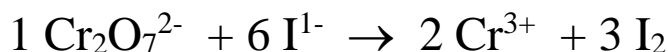
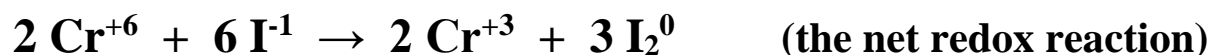
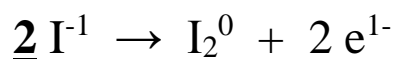
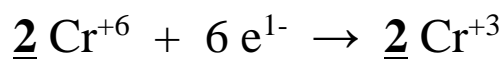
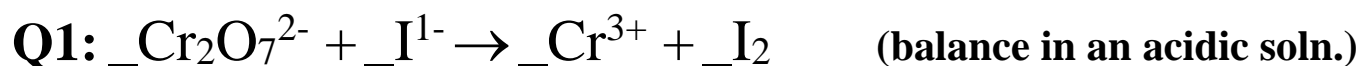
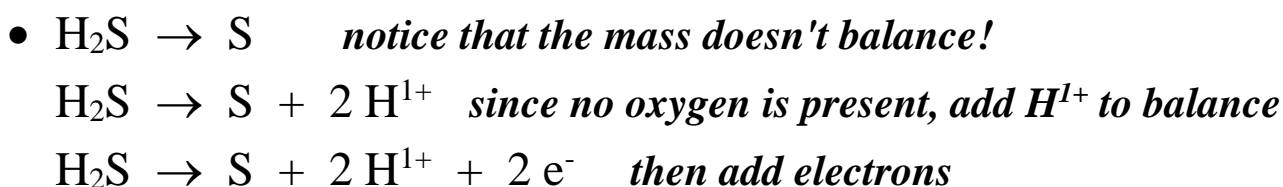
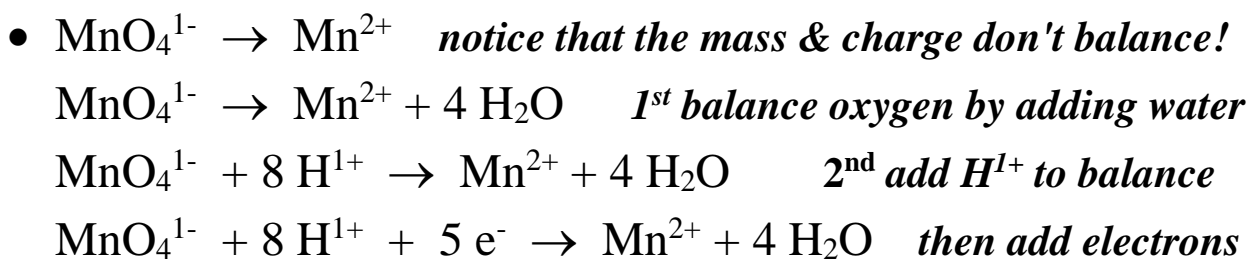
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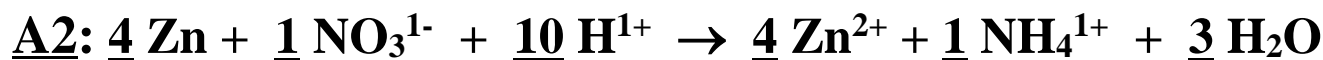
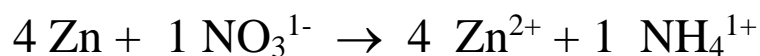
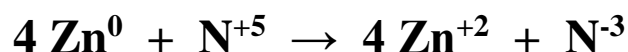
## Lesson-3

### II - Balancing Redox Reactions (Continued)

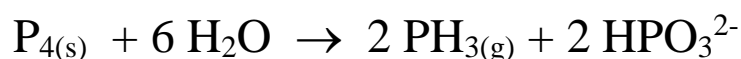
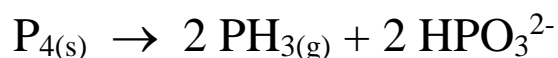
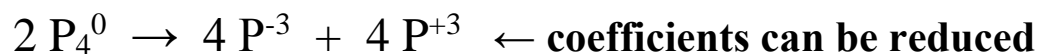
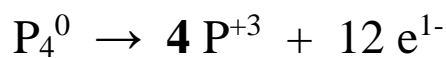
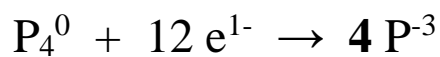
#### B) Reactions in acidic Solutions

- In a balanced half-reaction, the mass and charge must balance.
- In an acidic solution, reactions are balanced by using  $\text{H}_2\text{O}$  to balance oxygen atoms and then  $\text{H}^{1+}$  to balance hydrogen atoms.



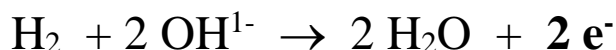
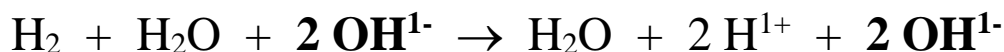
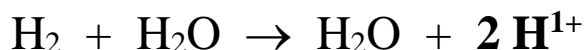
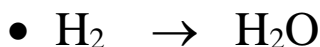
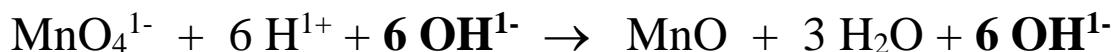
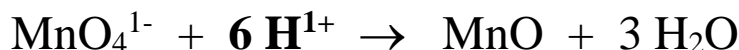
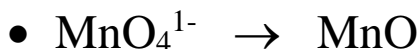


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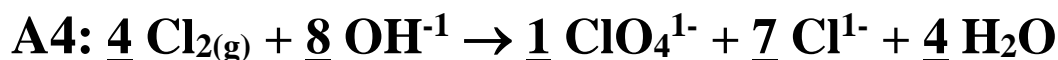
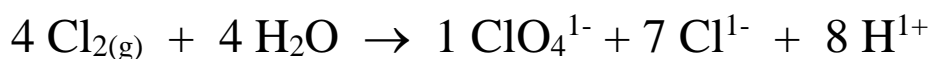
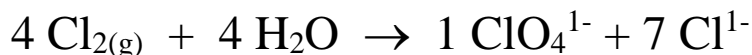
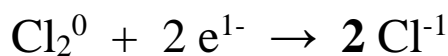


### C) Reactions in Basic Solutions

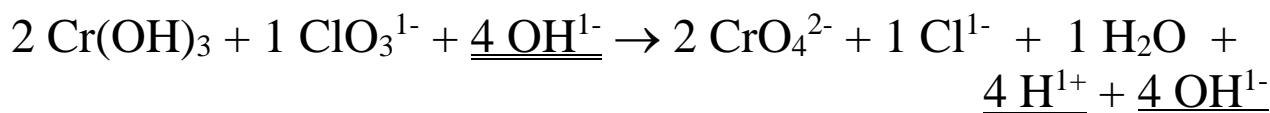
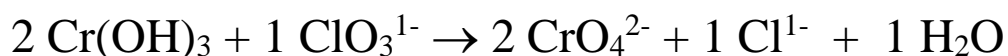
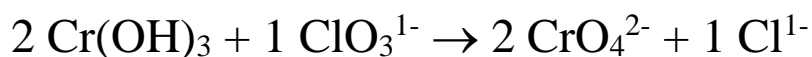
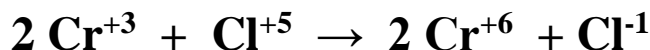
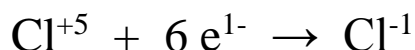
- In a basic solution, balance the reaction as you would an acidic solution, but then  $\text{OH}^{1-}$  to both sides to make the solution basic.



(in a basic solution)



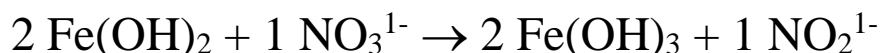
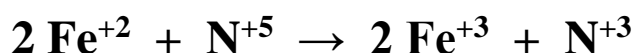
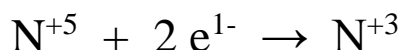
**Q5:**  $\_ \text{Cr}(\text{OH})_3 + \_ \text{ClO}_3^{1-} \rightarrow \_ \text{CrO}_4^{2-} + \_ \text{Cl}^{1-}$  (in a basic soln.)



**A5:**  $\underline{2} \text{Cr}(\text{OH})_3 + \underline{1} \text{ClO}_3^{1-} + \underline{4} \text{OH}^{1-} \rightarrow \underline{2} \text{CrO}_4^{2-} + \underline{1} \text{Cl}^{1-} + \underline{5} \text{H}_2\text{O}$   
odd b/c  $\text{H}^+$  added to same side as  $\text{H}_2\text{O}$

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**Q6:**  $\_ \text{Fe}(\text{OH})_2 + \_ \text{NO}_3^{1-} \rightarrow \_ \text{Fe}(\text{OH})_3 + \_ \text{NO}_2^{1-}$  (in a basic soln.)



**A6:**  $\underline{2} \text{Fe}(\text{OH})_2 + \underline{1} \text{NO}_3^{1-} + \underline{1} \text{H}_2\text{O} \rightarrow \underline{2} \text{Fe}(\text{OH})_3 + \underline{1} \text{NO}_2^{1-}$

odd b/c no  $\text{H}^+$  needs to be added thus no  $\text{OH}^-$  needs to be added.

# Chapter-20

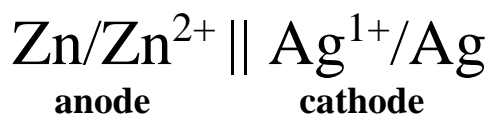
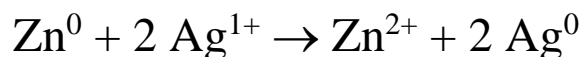
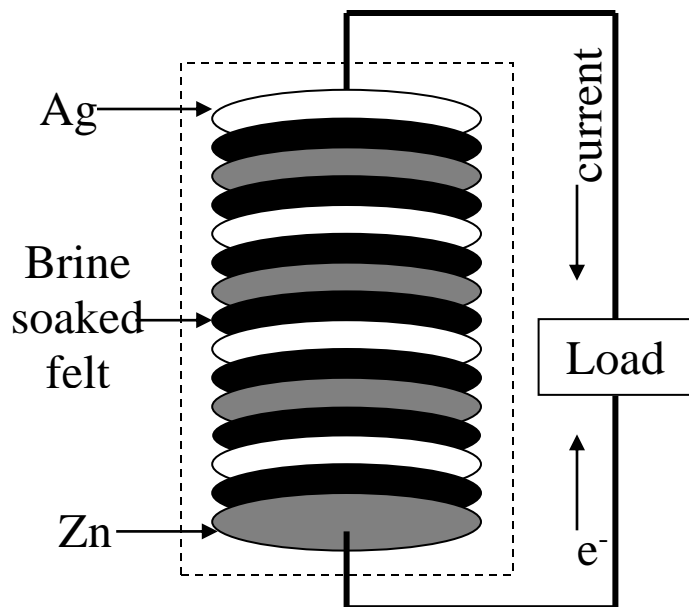
## Lesson-4

### III – Voltaic (Galvanic) Cells

- A **voltaic (galvanic) cell** is a device in which a spontaneous chemical reaction is used to produce electricity (ie. ***produce electrical work***).
- Oxidation always occurs at the anode (***an ox***).
- In a voltaic (galvanic) cell, the anode is negatively (–) charged.
- Reduction always occurs at the cathode (***red cat***).
- In a voltaic (galvanic) cell, the cathode is positively (+) charged.
- Anions move through a "connector" toward the anode.
- Cations move through a "connector" toward the cathode.
- Electrons move through the external wire/load toward the cathode.
- voltaic (galvanic) cells use the cell notation: **anode || cathode**

#### A) The Voltaic Pile:

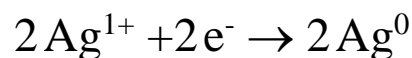
In 1799 Alessandro Volta invented the first source of steady electric current. It consisted of a stack of alternating zinc and silver disks separated by felt soaked in a brine solution.



**at anode (–):**

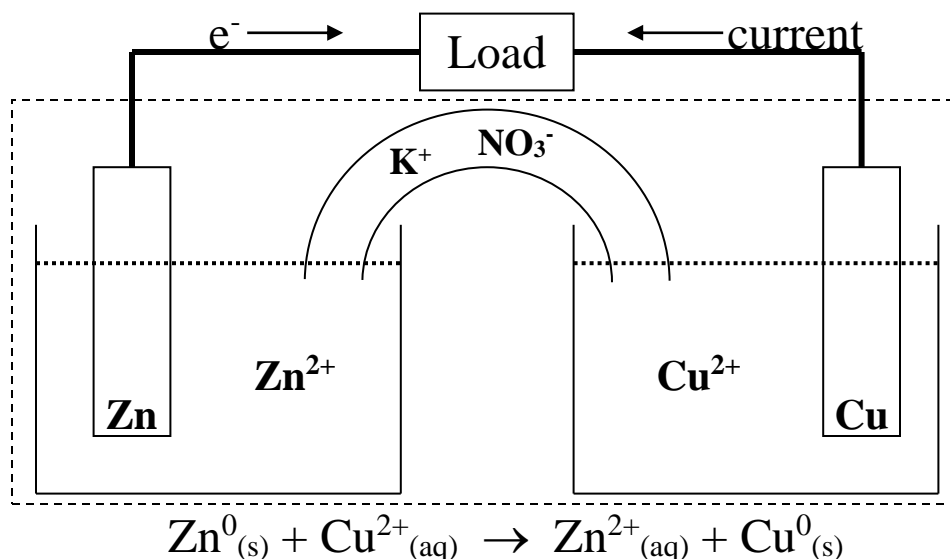


**at cathode (+):**



## B) The Daniell Cell:

In 1836 John Daniell invented the first reliable source of electric current.  **$\text{Zn}/\text{Zn}^{2+}||\text{Cu}^{2+}/\text{Cu}^0$**



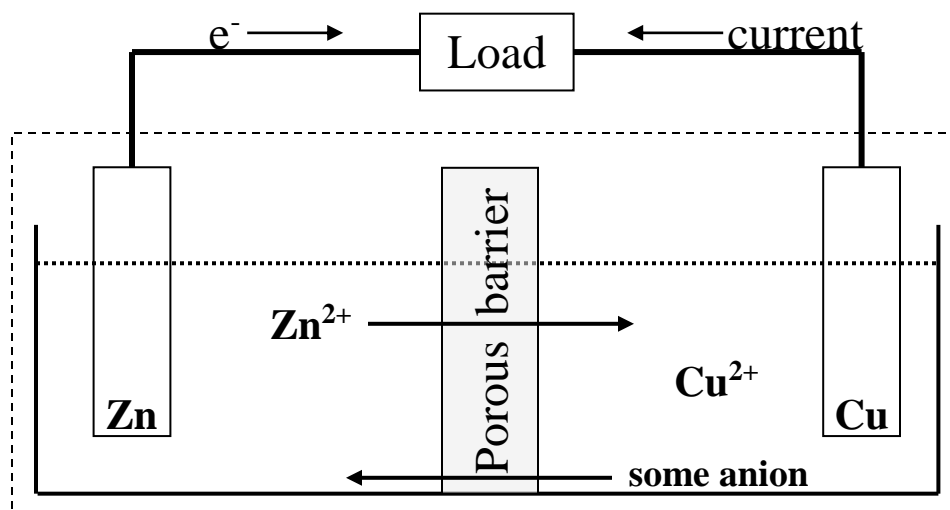
**at anode (-):**



**at cathode (+):**

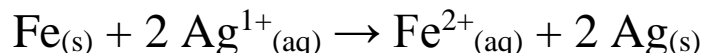


## C) The Need to Separate the Half-Reactions



If the half-reactions were not separated by a salt bridge or a porous barrier, then the electrons would be directly transferred from the reducing agent to the oxidizing agent and the potential for producing electrical work would be lost. However, the barrier must allow for the migration of ions between the half-cells in order to maintain the electrical neutrality of each half-cell. Without an appropriate ion flow, no electron flow occurs.

**Q1:** A voltaic cell (similar to the Daniell cell) is constructed of a silver strip placed in a solution of  $\text{AgNO}_3$  and an iron strip placed in a solution of  $\text{FeCl}_2$ . The net redox reaction that drives this cell is:



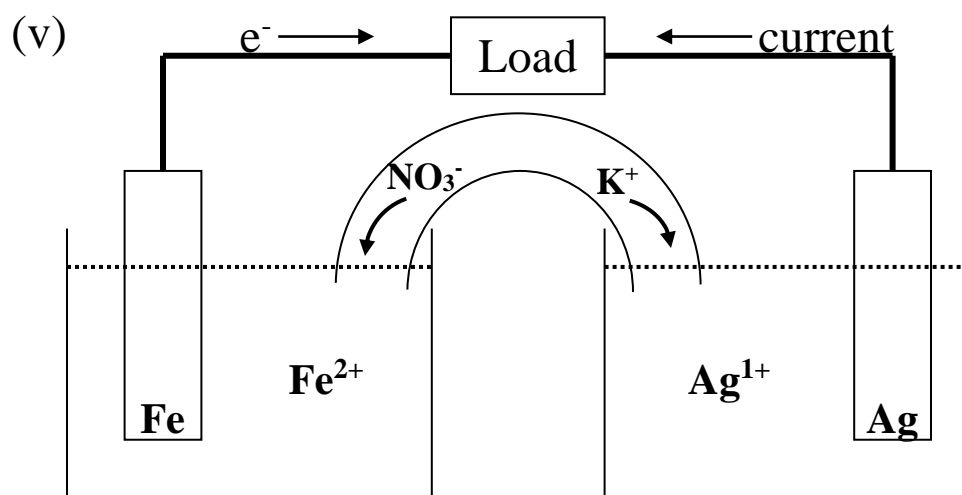
(i) What is being oxidized, and what is being reduced? (ii) Write the two half-reactions that occur in the two half-cells (electrode compartments). (iii) Which electrode is the anode and which is the cathode? (iv) What are the signs of the Ag and Fe electrodes? (v) Draw a diagram of the voltaic cell. (vi) on the diagram, indicate the direction of electron flow and current flow through the external wire. (vii) on the diagram, indicate the direction of ion flow through the salt bridge.

**A1:** (i)  $\text{Fe}_{(\text{s})}$  is being oxidized and  $\text{Ag}^{1+}_{(\text{aq})}$  is being reduced.



(iii)  $\text{Fe}_{(\text{s})}$  is the anode and  $\text{Ag}_{(\text{s})}$  is the cathode.

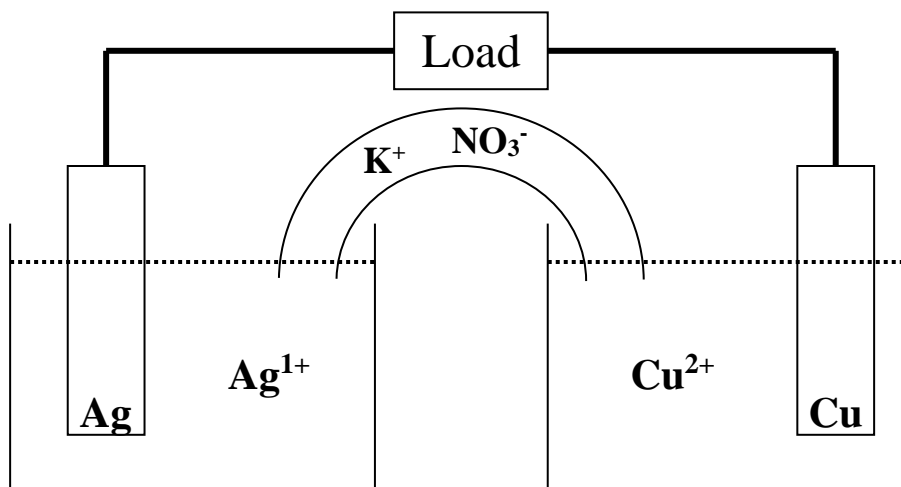
(iv)  $\text{Fe}_{(\text{s})}$  is negative (-) and  $\text{Ag}_{(\text{s})}$  is positive (+).



(vi) electrons flow from  $\text{Fe}_{(\text{s})}$  through the wire to  $\text{Ag}_{(\text{s})}$

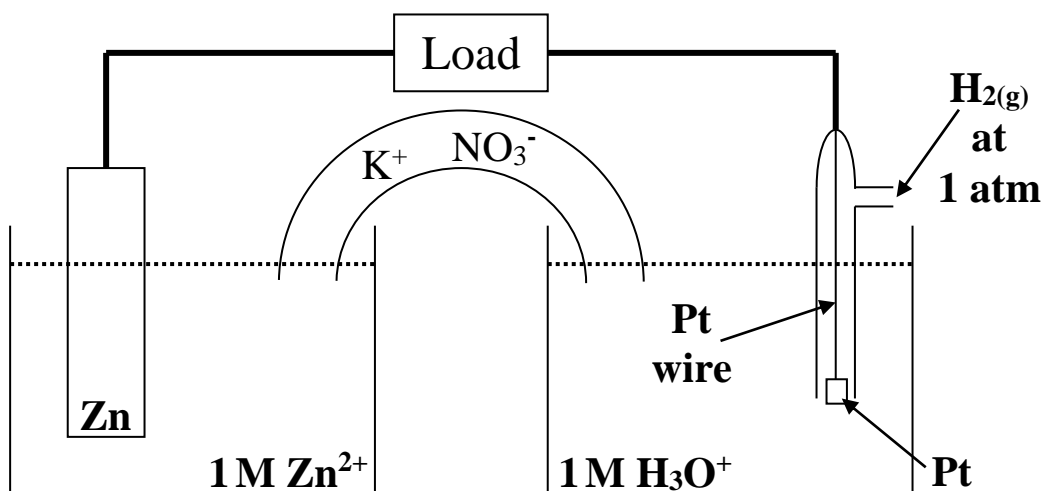
(vii)  $\text{K}^{1+}$  ions flow to the right and  $\text{NO}_3^{1-}$  ions flow to the left.

**Q2:** What is the cell notation for the following voltaic cell?



**A2:**  $\text{Cu}/\text{Cu}^{2+} \parallel \text{Ag}^+/\text{Ag}$

**Q3:** What is the cell notation for the following voltaic cell?



**A3:**  $\text{Zn}/\text{Zn}^{2+} \parallel (\text{Pt})\text{H}^+/\text{H}_2$

**Q4:** Why is platinum used at the hydrogen electrode?

**A4:** Hydrogen can not physically be the electrode, so an inert conductive material is used as the electrode.



# Chapter-20

## Lesson-5

### IV – Cell EMF under Standard Conditions

- The difference in PE (J) per electrical charge (C) between the two electrodes is called the **potential difference** and is measured in units of **volts**.

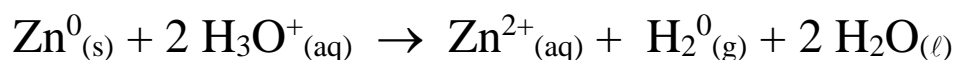
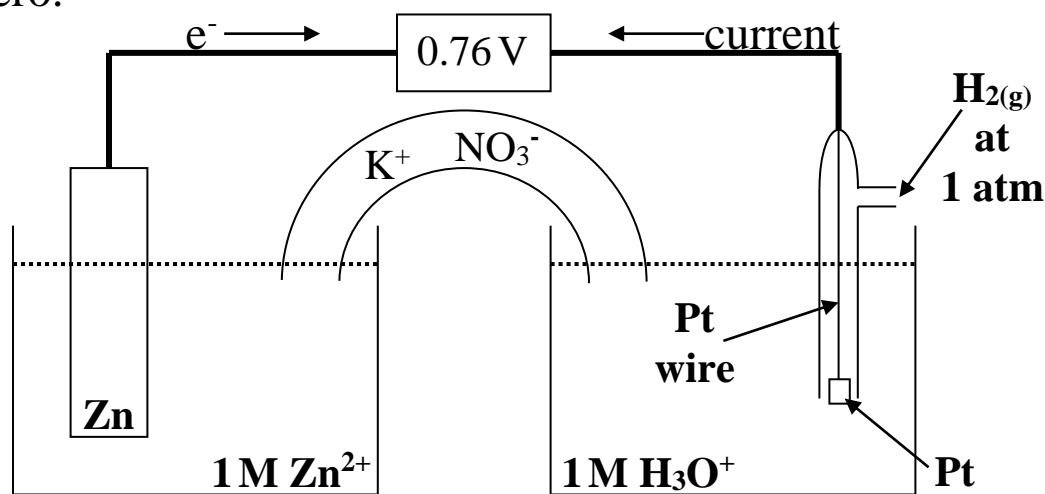
$$1\text{V} = 1 \frac{\text{J}}{\text{C}}$$

- 1 electron ( $e^-$ ) has an electrical charge equal to  **$-1.602 \times 10^{-19}$  C**.
- 1 mole of electrons has an electrical charge equal to  **$-96485$  C**.
- In a voltaic cell, the potential difference that **pushes** the electrons from one electrode through the external circuit to the second electrode is called the **electromotive force (EMF)**.

#### A) The Standard Hydrogen Electrode (Half-Cell):

- Standard conditions are defined as **1 M** for any aqueous solution and **1 atm** for any gas.
- The reduction reaction  $2 \text{H}^{1+}_{(\text{aq}, 1\text{M})} + 2 e^- \rightarrow \text{H}_{2(\text{g}, 1 \text{ atm})}$  was chosen as the reference half-reaction and assigned a standard reduction potential of zero volts (0 V).
- $E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}}$       or       $E^\circ_{\text{cell}} = E^\circ_{\text{red of cathode}} - E^\circ_{\text{red of anode}}$
- Thus,  $E^\circ_{\text{ox of anode}} = - E^\circ_{\text{red of anode}}$
- If  $E^\circ_{\text{cell}}$  for the reaction  $\text{Zn}_{(\text{s})} + 2 \text{H}^{1+}_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + \text{H}_{2(\text{g})}$  is  $+0.76 \text{ V}$ , and if  $E^\circ_{\text{red hydrogen}} = 0.00 \text{ V}$ , then  $E^\circ_{\text{ox zinc}} = +0.76 \text{ V}$
- $\text{Zn}^0 \rightarrow \text{Zn}^{2+} + 2 e^-$  has an  $E^\circ_{\text{ox}} = +0.76 \text{ V}$
- $\text{Zn}^{2+} + 2 e^- \rightarrow \text{Zn}^0$  has an  $E^\circ_{\text{red}} = -0.76 \text{ V}$
- Since the reaction in a voltaic cell must always be spontaneous, then the cell voltage must always be positive.

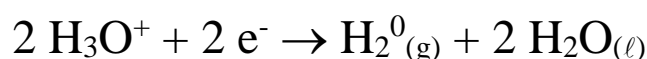
- The standard hydrogen electrode (SHE) was chosen as the standard reference electrode and assigned an electrode potential of zero.



**at anode (-):**



**at cathode (+):**



- The Zn is an **active electrode**. The Pt is an **inactive electrode**!

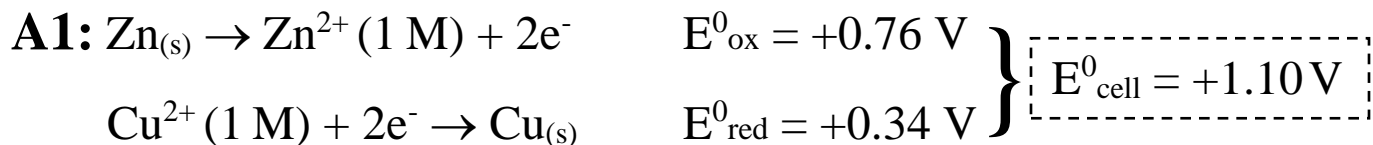
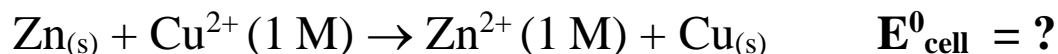
## B) Calculating Standard Cell Voltages:

- When reading a table of standard reduction potentials, several points must be remembered:
  - 1) The sign of the voltage must be reversed if the reaction is being read backwards.
  - 2) The magnitude of the voltage for a reaction remains the same even if the reaction is doubled, tripled, etc., because voltage is a ratio of the joules to the coulombs. Thus the ratio will always remain the same.
- The more positive the  $E^\circ_{\text{cell}}$ , the greater the net driving force of the cell.
- If the  $E^\circ_{\text{cell}}$  is negative, then the magnitude of the voltage is the minimum voltage necessary to drive the reaction.
- To find the  $E^\circ_{\text{cell}}$  of a reaction, simply find the  $E^\circ_{\text{red}}$  of the reduction half-reaction and the  $E^\circ_{\text{ox}}$  of the oxidation half-reaction and add them together. ***See Appendix E for reduction potentials.***

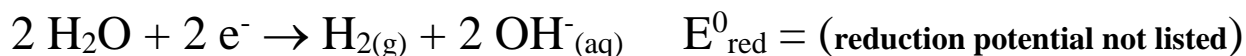
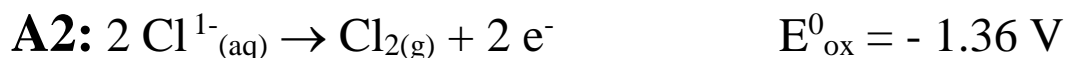
<u>Half Reaction</u>		<u>E° (V)</u>
$\text{F}_{2(\text{g})} + 2 \text{e}^- \rightarrow 2 \text{F}^{1-}$		2.87
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$		1.82
$\text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au}_{(\text{s})}$		1.50
$\text{Cl}_{2(\text{g})} + 2 \text{e}^- \rightarrow 2 \text{Cl}^{1-}$		1.36
$\text{O}_{2(\text{g})} + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}_{(\text{l})}$		1.23
$\text{Br}_{2(\text{l})} + 2 \text{e}^- \rightarrow 2 \text{Br}^{1-}$		1.07
$2 \text{Hg}^{2+} + 2 \text{e}^- \rightarrow \text{Hg}_2^{2+}$		0.92
$\text{Hg}^{2+} + 2 \text{e}^- \rightarrow \text{Hg}_{(\text{l})}$		0.85
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$		0.80
$\text{Hg}_2^{2+} + 2 \text{e}^- \rightarrow \text{Hg}_{(\text{l})}$		0.79
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$		0.77
$\text{I}_{2(\text{s})} + 2 \text{e}^- \rightarrow 2 \text{I}^{1-}$		0.53
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$		0.52
$\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$		0.34
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$		0.15
$\text{Sn}^{4+} + 2 \text{e}^- \rightarrow \text{Sn}^{2+}$		0.15
$\text{S}_{(\text{s})} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{S}_{(\text{g})}$		0.14
<b><math>2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})}</math></b>		<b>0.00</b>
$\text{Pb}^{2+} + 2 \text{e}^- \rightarrow \text{Pb}_{(\text{s})}$		-0.13
$\text{Sn}^{2+} + 2 \text{e}^- \rightarrow \text{Sn}_{(\text{s})}$		-0.14
$\text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}_{(\text{s})}$		-0.28
$\text{Co}^{2+} + 2 \text{e}^- \rightarrow \text{Co}_{(\text{s})}$		-0.28
$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}_{(\text{s})}$		-0.34
$\text{Cd}^{2+} + 2 \text{e}^- \rightarrow \text{Cd}_{(\text{s})}$		-0.40
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$		-0.41
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}_{(\text{s})}$		-0.74
$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}_{(\text{s})}$		-0.44
$\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}_{(\text{s})}$		-0.76
$2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{1-}_{(\text{aq})}$		-0.83
$\text{Mn}^{2+} + 2 \text{e}^- \rightarrow \text{Mn}_{(\text{s})}$		-1.18
$\text{Al}^{3+} + 3 \text{e}^- \rightarrow \text{Al}_{(\text{s})}$		-1.66
$\text{Be}^{2+} + 2 \text{e}^- \rightarrow \text{Be}_{(\text{s})}$		-1.70
$\text{Mg}^{2+} + 2 \text{e}^- \rightarrow \text{Mg}_{(\text{s})}$		-2.37
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}_{(\text{s})}$		-2.71
$\text{Ca}^{2+} + 2 \text{e}^- \rightarrow \text{Ca}_{(\text{s})}$		-2.87
$\text{Sr}^{2+} + 2 \text{e}^- \rightarrow \text{Sr}_{(\text{s})}$		-2.89
$\text{Ba}^{2+} + 2 \text{e}^- \rightarrow \text{Ba}_{(\text{s})}$		-2.90
$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}_{(\text{s})}$		-2.92
$\text{K}^+ + \text{e}^- \rightarrow \text{K}_{(\text{s})}$		-2.92
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}_{(\text{s})}$		-2.92
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}_{(\text{s})}$		-3.05

*A more complete table of reduction potentials is found on page 1128 in your textbook*

**Q1:** What is the  $E^0_{\text{cell}}$  for the reaction,



**Q2:** What is the  $E^0_{\text{red}}$  for the following reaction if the  $E^0_{\text{cell}} = -2.19 \text{ V}$ ?

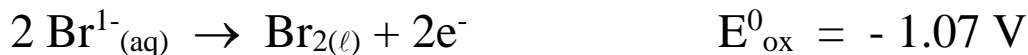
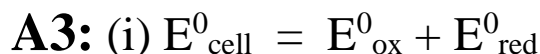


$$E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}}$$

$$E^0_{\text{red}} = (-2.19 \text{ V}) - (-1.36 \text{ V}) \rightarrow E^0_{\text{red}} = -0.83 \text{ V}$$



**Q3:** (i) Determine the total cell voltage for the following reaction and then (ii) determine the reaction's spontaneity.



$$E^0_{\text{cell}} = (-1.07 \text{ V}) + (-0.83 \text{ V}) = -1.90 \text{ V}$$

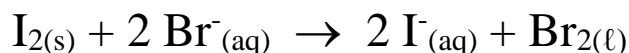
(ii) The reaction is nonspontaneous. A minimum voltage of 1.90 V must be applied to force the reaction to occur.

**Q4:** Determine the reaction that **spontaneously** occurs between the following reactants.

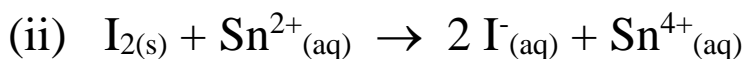
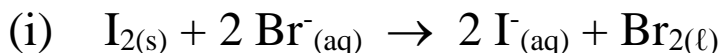
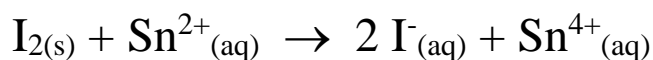


**A4:** Consider all the possible reactions!  $\text{I}_2$  is a strong oxidizing agent.

(i) *In redox reactions, halogens often react with each other*



(ii) *In redox reactions, halogens sometimes react with metallic ions that can gain oxidation number.*



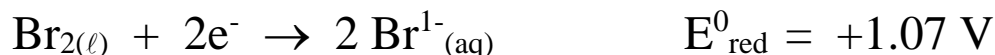
**Reaction-ii is the one that takes place spontaneously.**

**Your knowledge of the halogen activity series would alert you that reaction-i would be nonspontaneous.**

**Q5:** (i) Determine the total cell voltage for the following reaction and then (ii) determine the reaction's spontaneity.



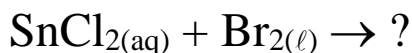
**A5:** (i)  $E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}}$



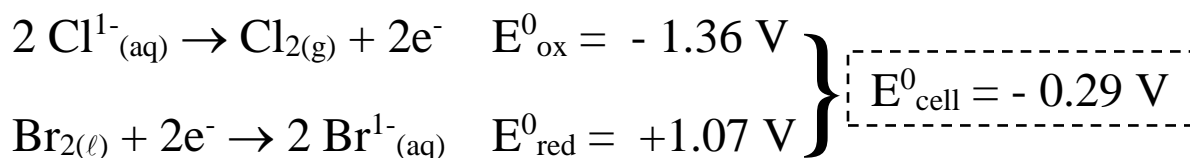
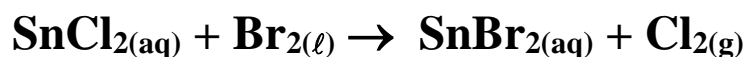
$$E^0_{\text{cell}} = (+0.25 \text{ V}) + (+1.07 \text{ V}) = \boxed{+1.35 \text{ V}}$$

(ii) The reaction is spontaneous.

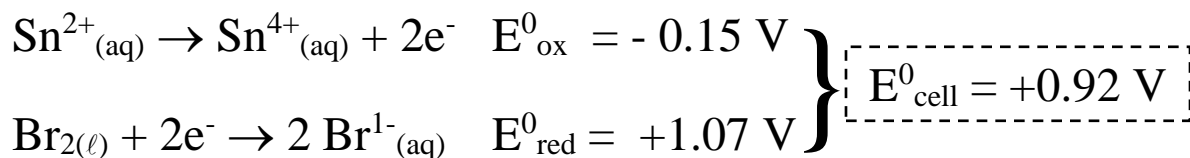
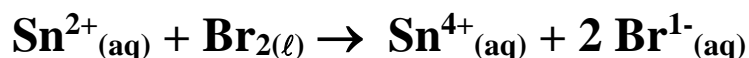
**Q6:** Determine the reaction that **spontaneously** occurs between the following reactants.



**A6:** Consider all the possible reactions!



**THIS IS NOT THE SPONTANEOUS REACTION!**



**THIS IS THE SPONTANEOUS REACTION!**

# Chapter-20

## Lesson-6

### V – Free Energy and Redox Reactions

#### A) $E^0_{\text{cell}}$ and $\Delta G^0$

- When  $E^0_{\text{cell}} > \text{zero}$ , the reaction is spontaneous.
- When  $\Delta G^0 < \text{zero}$ , the reaction is spontaneous.
- Thus  $E^0_{\text{cell}}$  must be related to  $\Delta G$ .

$$\Delta G^0 = -nFE^0_{\text{cell}} \quad (n = \text{moles of transferred electrons})$$

when  $\Delta G$  is in kJ,  $F$  is 96.485 kJ/V•mol, but ...

when  $\Delta G$  is in joules,  $F$  is 96485 J/V•mol.

#### **WATCH YOUR UNITS!**

- $F$  is the symbol for Faraday's constant which is the amount of electrical charge found on one mole of electrons.

**1 mole of electrons = 96485 coulombs**

**Q1:** If the  $E^0_{\text{cell}}$  for the reaction  $2\text{Na}_{(\text{s})} + 2\text{HOH}_{(\ell)} \rightarrow 2\text{NaOH}_{(\text{aq})} + \text{H}_{2(\text{g})}$  is +1.88 V, then calculate the  $\Delta G^0$ .

**A1:**  $\Delta G^0 = -n F E^0_{\text{cell}}$

$$\Delta G^0 = -(2)(96.485)(+1.88) \rightarrow \boxed{\Delta G^0 = - 363 \text{ kJ}}$$

**Q2:** When Cd metal reduces  $\text{Cu}^{2+}$  ions in solution, Cu metal and  $\text{Cd}^{2+}$  ions form. If the  $\Delta G$  for the reaction is - 143 kJ, then calculate the  $E^0_{\text{cell}}$ .

**A2:**  $\Delta G^0 = -n F E^0_{\text{cell}}$

$$- 143 = -(2)(96.485)(E^0_{\text{cell}}) \rightarrow \boxed{E^0_{\text{cell}} = +0.741 \text{ V}}$$

B)  $E^0_{\text{cell}}$  and K

- At equilibrium, the  $E_{\text{cell}}$  is equal to zero thus...

$$E^0_{\text{cell}} = \frac{RT}{nF} \ln K \quad (\text{at } 25^\circ\text{C})$$

- When  $E^0_{\text{cell}} > \text{zero}$ , then  $K > 1$ . When  $E^0_{\text{cell}} < \text{zero}$ , then  $K < 1$ .

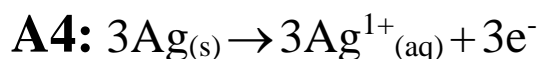
**Q3:** If the  $E^0_{\text{cell}}$  for the reaction  $\text{Cl}_{2(\text{g})} + 2 \text{Br}^{1-}_{(\text{aq})} \rightarrow 2 \text{Cl}^{1-}_{(\text{aq})} + \text{Br}_{2(\ell)}$  is +0.29 V, then calculate the value of the equilibrium constant for the reaction at  $25^\circ\text{C}$ ?

**A3:**  $E^0_{\text{cell}} = [RT/n F] \ln K$

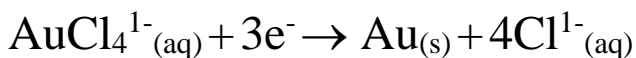
$$+0.29 = [(8.314)(298)/(2)(96485)] \ln K$$

$$\boxed{K = 6.4 \times 10^9}$$

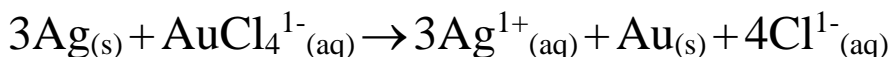
**Q4:** Calculate the  $E^0_{\text{cell}}$ ,  $\Delta G^0$ , and  $K_{\text{eq}}$  at  $25^\circ\text{C}$  for the following redox reaction.



$$E^0_{\text{ox}} = -0.80 \text{ V}$$



$$+ E^0_{\text{red}} = +1.00 \text{ V}$$



$$\boxed{E^0_{\text{cell}} = +0.20 \text{ V}}$$

$$\Delta G^0 = -n F E^0_{\text{cell}}$$

$$\Delta G^0 = -(3)(96.485)(+0.20)$$

$$\boxed{\Delta G^0 = -58 \text{ kJ}}$$

$$E^0_{\text{cell}} = [RT/n F] \ln K$$

$$+0.20 = [(8.314)(298)/(3)(96485)] \ln K$$

$$\boxed{K = 1.4 \times 10^{10}}$$



**Q5:** How many moles of electrons are being transferred in a redox reaction whose  $E^0_{\text{cell}} = +0.93$  and whose  $\Delta G = -180 \text{ kJ}$ ?

**A5:**  $\Delta G^0 = -n F E^0_{\text{cell}}$

$$-180 = -(n)(96.485)(+0.93) \rightarrow \boxed{n = 2 \text{ moles } e^-}$$

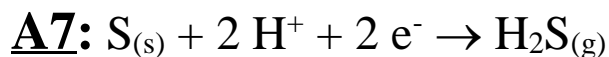
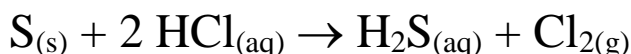
**Q6:** If the  $E^0_{\text{cell}}$  for the reaction  $\text{Cu}_{(\text{s})} + \text{Sn}^{2+}_{(\text{aq})} \rightarrow \text{Cu}^{2+}_{(\text{aq})} + \text{Sn}_{(\text{s})}$  is  $-0.473 \text{ V}$ , then calculate the value of the equilibrium constant for the reaction at  $25^\circ\text{C}$ ?

**A6:**  $E^0_{\text{cell}} = [RT/n F] \ln K$

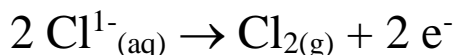
$$-0.473 = [(8.314)(298)/(2)(96485)] \ln K$$

$$\boxed{K = 1.00 \times 10^{-16}}$$

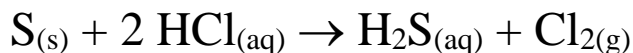
**Q7:** Calculate the  $E^0_{\text{cell}}$ ,  $\Delta G^0$ , and  $K_{\text{eq}}$  at  $25^\circ\text{C}$  for the following redox reaction.



$$E^0_{\text{ox}} = +0.14 \text{ V}$$



$$+ \quad E^0_{\text{red}} = -1.36 \text{ V}$$



$$\boxed{E^0_{\text{cell}} = -1.22 \text{ V}}$$

$$\Delta G^0 = -n F E^0_{\text{cell}}$$

$$\Delta G^0 = -(2)(96.485)(-1.22)$$

$$\boxed{\Delta G^0 = +235 \text{ kJ}}$$

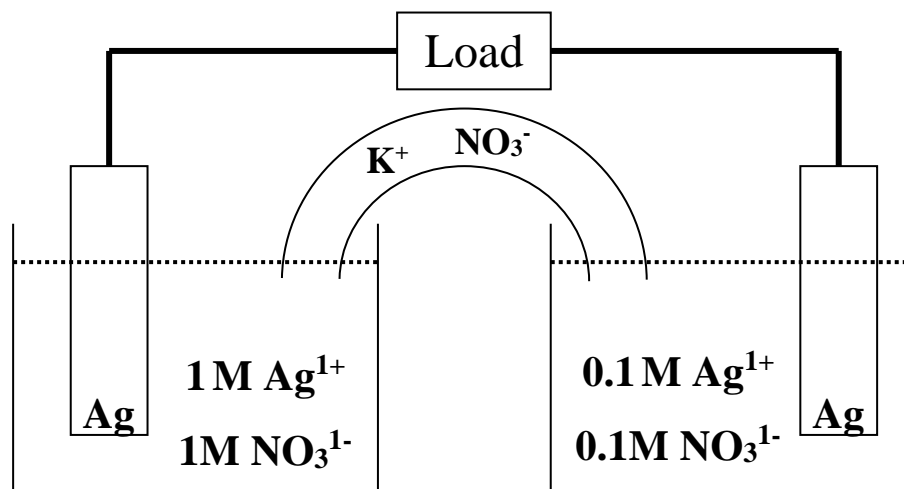
$$E^0_{\text{cell}} = [RT/n F] \ln K$$

$$-1.22 = [(8.314)(298)/(2)(96485)] \ln K$$

$$\boxed{K = 5.40 \times 10^{-42}}$$

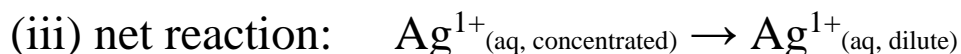
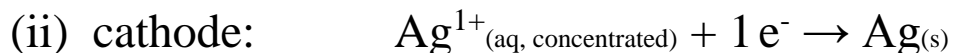
## VI – Concentration Cells

- A galvanic (voltaic) cell in which both half-cells contain the same metal but whose ionic solutions have a different concentration are called **concentration cells**. (See diagram below.)



- When the ionic concentrations of two half-cells of the same ionic electrolyte are different, a spontaneous reaction occurs in order to equalize the two concentrations.
- In order to reduce the concentration of the  $\text{Ag}^{1+}$  ions in the half-cell on the left (See diagram above) reduction must occur and in order to increase the concentration of the  $\text{Ag}^{1+}$  ions in the half-cell on the right (See diagram above) oxidation must occur.
- Thus, in a concentration cell, the high concentration half-cell is the cathode cell and the low concentration half-cell is the anode cell.

**Q8:** For the concentration cell above, (i) write the half reaction that occurs at the anode, (ii) write the half reaction that occurs at the cathode, (iii) write the net reaction, and state the direction that electrons are flowing through the external wire.



(iv) Electrons flow from right to left through the external wire.

# Chapter-20

## Lesson-7

### VII – Cell EMF under Nonstandard Conditions

#### A) Qualitative Effect

- Voltage is a measure of the spontaneity of a reaction.
- Voltage is increased by increasing the concentrations of the reactants or by decreasing the concentration of the products. (Le Chatelier's Principle)
- Voltage is decreased by decreasing the concentrations of the reactants or by increasing the concentration of the products. (Le Chatelier's Principle)
- For the reaction,  $\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

and as the reaction proceeds to equilibrium, Q increases and thus voltage decreases. At equilibrium the voltage is zero!

Thus as the  $Q \uparrow$ , the  $E_{\text{cell}} \downarrow$

**Q1:** The following voltaic cell,  $[\text{Co}_{(s)}/(1.0\text{M})\text{Co}^{2+}|| (1.0\text{M})\text{Pb}^{2+}/\text{Pb}_{(s)}]$  has an initial voltage of +0.15 V. If the initial conditions of the cell are modified to be  $[\text{Co}_{(s)}/(0.0010\text{M})\text{Co}^{2+}|| (1.0\text{M})\text{Pb}^{2+}/\text{Pb}_{(s)}]$ , then the initial voltage of the cell will be...

**A1:** ...greater than +0.15 V! Since  $Q = [\text{Co}^{2+}]/[\text{Pb}^{2+}]$ , then a decrease in the concentration of  $\text{Co}^{2+}$  will decrease the initial value of Q which in turn will give the cell a voltage greater than +0.15 V.

## B) Quantitative Effect

- The Nernst equation is used to quantitatively determine the effect of concentration on voltage.

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$E^0_{\text{cell}}$  = standard voltage

$R = 8.314 \text{ J/mol}\cdot\text{K}$

$T = \text{temp (K)}$

$n = \# \text{ moles of electrons transferred}$

$F = \text{Faraday's constant (96480 C/mol)}$

$Q = \text{reaction quotient (note at equilibrium } Q \text{ would be } K_{eq})$

**Q2:** The following voltaic cell,  $[\text{Co}_{(s)}/(1.0\text{M})\text{Co}^{2+}|| (1.0\text{M})\text{Pb}^{2+}/\text{Pb}_{(s)}]$  has an initial voltage of +0.15 V. If the initial conditions of the cell are modified to be  $[\text{Co}_{(s)}/(0.0010\text{M})\text{Co}^{2+}|| (1.0\text{M})\text{Pb}^{2+}/\text{Pb}_{(s)}]$ , then the initial voltage of the cell at 25°C will be...

**A2:**  $E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$   $Q = [\text{Co}^{2+}]/[\text{Pb}^{2+}]$

$$E_{\text{cell}} = +0.15 - [(8.314)(298)/(2)(96485)]\ln([0.0010]/[1.0])$$

$E_{\text{cell}} = +0.24 \text{ V}$

**Q3:** Calculate the voltage for the concentration cell in which one half-cell contains an Ag electrode in a 1.0 M  $\text{AgNO}_3$  solution and the other half-cell contains an Ag electrode in a  $1.0 \times 10^{-3}$  M  $\text{AgNO}_3$  solution at 293 K

**A3:**  $\text{Ag}^{1+}_{(\text{aq, concentrated})} \rightarrow \text{Ag}^{1+}_{(\text{aq, dilute})}$   $Q = [\text{Ag}^{1+}_{\text{dilute}}]/[\text{Ag}^{1+}_{\text{conc.}}]$

$$E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$$

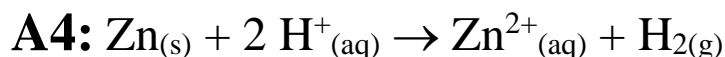
$$E_{\text{cell}} = +0.00 - \frac{(R)(T) \cdot \ln [\text{Ag}^{1+}_{\text{dilute}}]}{(n)(F) [\text{Ag}^{1+}_{\text{conc.}}]}$$

$$E_{\text{cell}} = +0.00 - \frac{(8.314)(273) \cdot \ln [0.0010]}{(1)(96485) [1.00]} \rightarrow \boxed{E_{\text{cell}} = +0.16 \text{ V}}$$

### C) Using the Nernst Equation to Determine Ion Conc.

- The most important use of the Nernst equation is the experimental determination of the concentration of a particular ion in a cell.

**Q4:** What is the concentration of  $H^+$  in the following cell at  $25^\circ C$  whose cell voltage is  $+0.20\text{ V}$ ?  $Zn_{(s)}/Zn^{2+}(1.0\text{ M})||H^+(? \text{ M})/H_{2(g)}(1.0\text{ atm})$



$$E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$$

$$+0.20 = +0.76 - \frac{[(8.314)(298)]}{(2)(96485)} \times \ln \frac{[1.0](1.0)}{[X]^2}$$

$$+0.56 = (0.0128) \times \ln \frac{1}{[X]^2} \quad \text{fyi} \rightarrow \ln 1/[X]^2 = \ln [X]^{-2}$$

$$+0.56 = (0.0128) \times \ln [X]^{-2} \quad \text{fyi} \rightarrow \ln [X]^{-2} = -2 \ln [X]$$

$$+0.56 = (0.0128) \times -2 \ln [X]$$

$$\boxed{X = 3.2 \times 10^{-10} \text{ M } H^+}$$

**Q5:** The reaction  $2 Ag_{(s)} + Cu^{2+}_{(aq)} \rightarrow 2 Ag^+_{(aq)} + Cu_{(s)}$  in a cell has a  $E^0_{\text{cell}} = -0.46\text{ V}$ . If  $[0.10\text{ M}] Cl^{1-}$  ions are added to the  $[Ag]/[Ag^+]$  half-cell so that the  $E_{\text{cell}}$  becomes  $+0.06\text{ V}$  then (i) calculate the new  $[Ag^+]$  at  $25^\circ C$  and (ii) calculate the  $K_{\text{sp}}$  of  $AgCl$ .

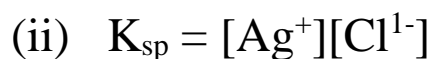


$$+0.06 = -0.46 - [(8.314)(298)/(2)(96485)] \ln ([X]^2/[1.0])$$

$$+0.52 = -(0.0128) \ln X^2 \quad \text{fyi} \rightarrow \ln X^2 = 2 \ln X$$

$$+0.52 = -(0.0256) \ln X$$

$$\boxed{X = 1.6 \times 10^{-9} \text{ M } Ag^+}$$



$$K_{\text{sp}} = [1.5 \times 10^{-9}][0.10] \rightarrow \boxed{K_{\text{sp}} = 1.5 \times 10^{-10}}$$

**Student Activity-6: Equilibrium Changes in a Voltaic Cell**

**Q6:** The following voltaic cell,  $[\text{Zn}_{(s)}/(1.0\text{M})\text{Zn}^{2+}|| (1.0\text{M})\text{Cu}^{2+}/\text{Cu}_{(s)}]$  has an initial voltage of +1.10 V. If the conditions of the cell have changed so that  $[\text{Zn}_{(s)}/(1.5\text{M})\text{Zn}^{2+}|| (0.5\text{M})\text{Cu}^{2+}/\text{Cu}_{(s)}]$ , then  
(i) calculate the new cell voltage and then  
(ii) predict the direction toward which the system has shifted.

**A6:** (i)  $E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$   $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$

$$E_{\text{cell}} = +1.10 - [(8.314)(298)/(2)(96485)]\ln([1.5]/[0.5])$$

$$E_{\text{cell}} = +1.09 \text{ V}$$

(ii) The system has shifted to the right.

**Q7:** The reaction  $2 \text{Al}_{(s)} + 3 \text{Sn}^{2+}_{(\text{aq})} \rightarrow 2 \text{Al}^{3+}_{(\text{aq})} + 3 \text{Sn}_{(s)}$  has a  $E^0_{\text{cell}}$  equal to +1.52 V. If some  $\text{Na}_3\text{PO}_{4(s)}$  is added to the  $[\text{Al}]/[\text{Al}^{3+}]$  half-cell so that the  $E_{\text{cell}}$  suddenly increases to +1.55 V, then  
(i) calculate the new  $[\text{Al}^{3+}]$  at 25°C and then  
(ii) predict the direction that the equilibrium will now shift.

**A7:** (i)  $E_{\text{cell}} = E^0_{\text{cell}} - (RT/nF)\ln Q$   $Q = [\text{Al}^{3+}]^2/[\text{Sn}^{2+}]^3$

$$+1.55 = +1.52 - [(8.314)(298)/(6)(96485)]\ln([X]^2/[1.0]^3)$$

$$0.03 = -[0.00428]\ln([X]^2)$$

$$0.03 = -(0.00428)\ln X^2 \quad \text{fyi} \rightarrow \ln X^2 = 2\ln X$$

$$0.03 = -(0.00856)\ln X$$

$$X = 0.03 \text{ M Al}^{3+}$$

(ii) The equilibrium will now shift to the right.

# Chapter-20

## Lesson-8

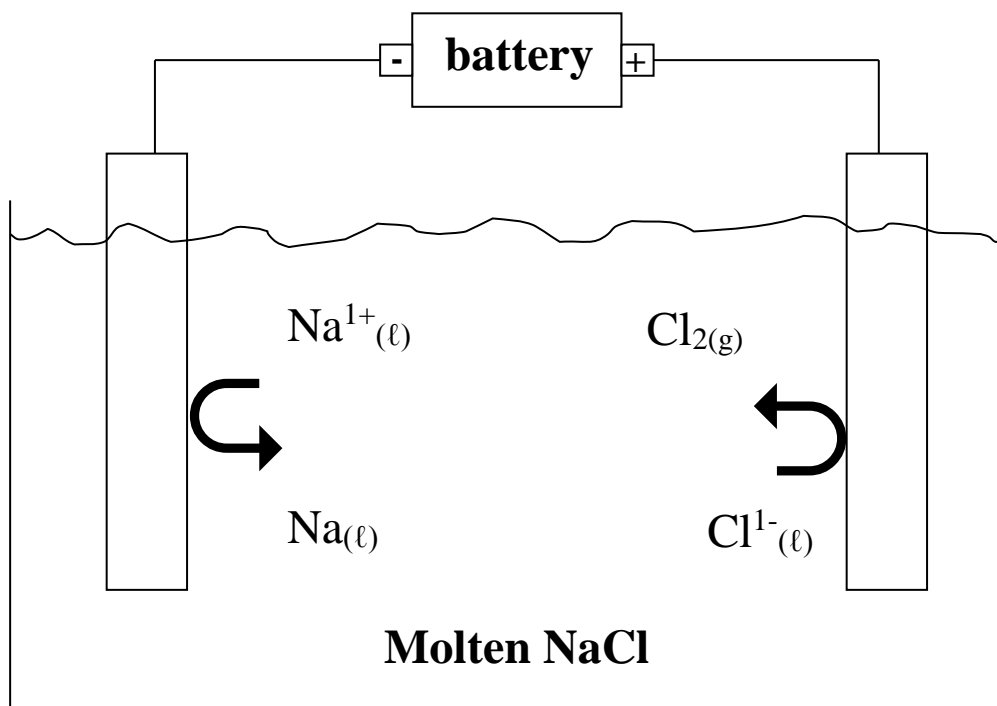
### VIII – Electrolysis and the Electrolytic Cell

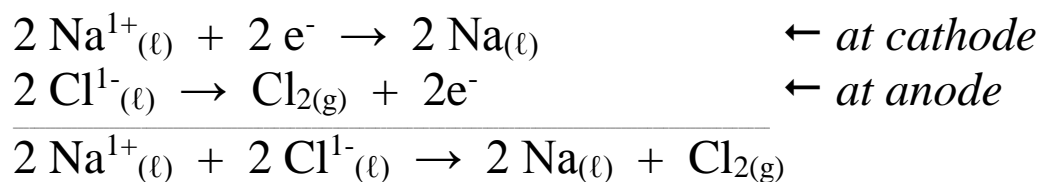
- **Electrolysis** is reaction in which a nonspontaneous redox reaction is brought about by the use of sufficient electric current.
- An **electrolytic cell** is a device that uses electrical energy to bring about an electrolysis reaction.

#### A) The Electrolytic Cell

- In an electrolytic cell, oxidation occurs at the anode (**an ox**) which is positively (+) charged.
- In an electrolytic cell, reduction occurs at the cathode (**red cat**) which is negatively (–) charged.
- Anions move through the cell toward the anode.
- Cations move through the cell toward the cathode.
- Electrons move through the external wire toward the cathode.
- An electrolytic cell requires an ***outside*** energy source!

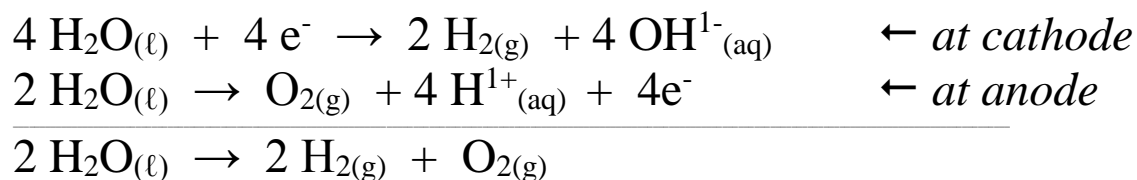
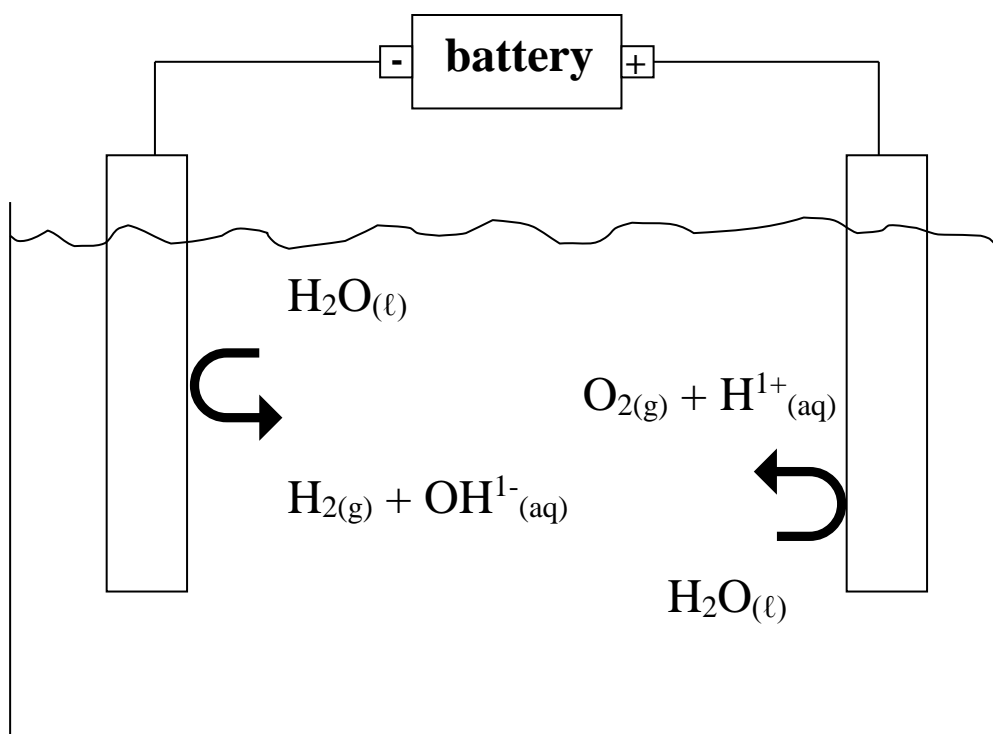
#### 1) Electrolysis of Pure Molten Salts:





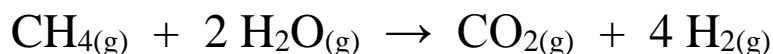
The chlorine gas bubbles out and pure molten sodium remains. The electrodes in this electrolytic cell are ***inactive***. They do not undergo reaction but only serve as the site for reduction and oxidation.

## 2) Electrolysis of Water:



***A small amount of an electrolyte is needed to carry the current.***

*The production of hydrogen gas and oxygen gas via electrolysis is very expensive. Most commercial hydrogen is produced by reacting methane gas with steam at 1100°C.*

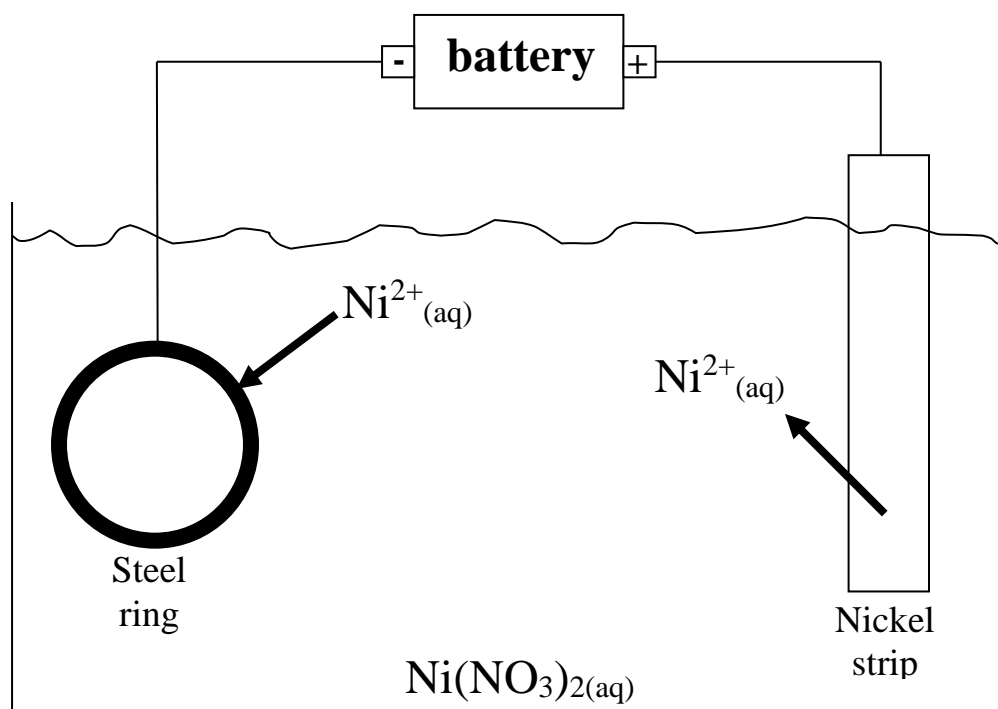


*Most commercial oxygen gas is prepared through the distillation of air.*



### 3) Electroplating:

- **Electroplating** occurs in an electrolytic cell.
- When electroplating, the electrodes are **active**.
- The material to be electroplated is the **cathode** and must be connected to the negative pole of the electric source.
- The electroplating metal is the **anode** and must be connected to the positive pole of the electric source
- An electrolyte containing the cation of the electroplating metal is required. *One that is soluble with an inactive anion is best.*



### B) Electrolysis in Aqueous Solutions

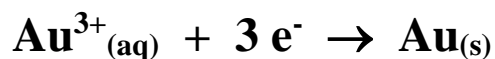
The electrolysis of aqueous solutions is complicated by the presence of water. Either the electrolyte, the water, or both will undergo electrolysis depending on which species is more easily oxidized and reduced.

The electrolysis of aqueous "MX" has four possible outcomes:

- 1) Pure M at the cathode and pure X at the anode
- 2) Pure M at the cathode and pure  $\text{O}_2$  at the anode
- 3) Pure  $\text{H}_2$  at the cathode and pure X at the anode
- 4) Pure  $\text{H}_2$  at the cathode and pure  $\text{O}_2$  at the anode

1) Reduction (at the cathode):

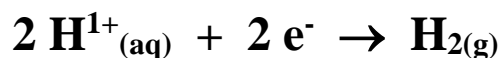
- a) All metallic cations are reduced to pure metals, *except for Group-1, Group-2, or aluminum cations.*



- b) *In the presence of Group-1, Group-2, and aluminum cations, water molecules are reduced to hydrogen gas (H<sub>2</sub>).*

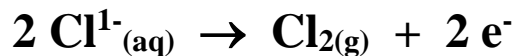
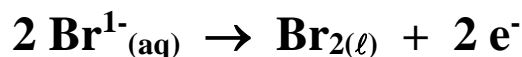
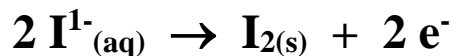


- c) *In the presence of a strong acid, hydrogen ions (H<sup>1+</sup>) are reduced to hydrogen gas (H<sub>2</sub>).*

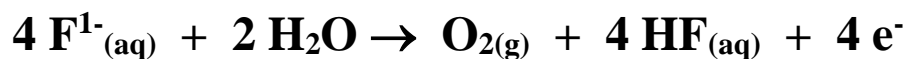
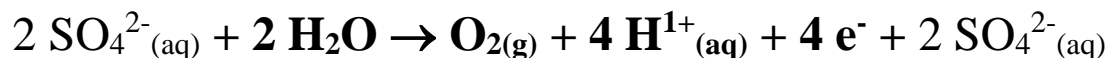
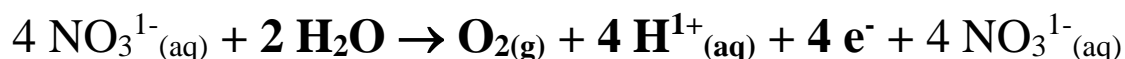


2) Oxidation (at the anode):

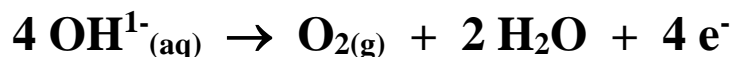
- a) Monoatomic nonmetallic anions are oxidized to pure non-metals, *except for fluoride.*



- b) *In the presence of fluoride or oxyanions of strong acids, water molecules are oxidized to oxygen gas (O<sub>2</sub>).*



- c) *In the presence of a strong base, hydroxide ions (OH<sup>1-</sup>) are oxidized to oxygen gas (O<sub>2</sub>).*



**Q1:** What are the products of the electrolysis of aqueous  $\text{NiCl}_2$ ?

**A1:** at the cathode:  $\text{Ni}_{(\text{s})}$   $(\text{Ni}^{2+}_{(\text{aq})} + 2 \text{e}^{-} \rightarrow \text{Ni}_{(\text{s})})$

at the anode:  $\text{Cl}_{2(\text{g})}$   $(2 \text{Cl}^{-}_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2 \text{e}^{-})$

Reaction:  $\text{Ni}^{2+}_{(\text{aq})} + 2 \text{Cl}^{-}_{(\text{aq})} \rightarrow \text{Ni}_{(\text{s})} + \text{Cl}_{2(\text{g})}$

**Q2:** What are the products of the electrolysis of aqueous  $\text{NaCl}$ ?

**A2:** at the cathode:  $\text{H}_{2(\text{g})}$  &  $\text{OH}^{-}_{(\text{aq})}$   $(2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^{-} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{-}_{(\text{aq})})$

at the anode:  $\text{Cl}_{2(\text{g})}$   $(2 \text{Cl}^{-}_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2 \text{e}^{-})$

Reaction:  $2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{Cl}^{-}_{(\text{aq})} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{-}_{(\text{aq})} + \text{Cl}_{2(\text{g})}$

**Q3:** What are the products of the electrolysis of **very dilute**  $\text{NaCl}_{(\text{aq})}$ ?

**A3:** at the cathode:  $\text{H}_{2(\text{g})}$  &  $\text{OH}^{-}_{(\text{aq})}$   $(2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^{-} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{-}_{(\text{aq})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}^{+}_{(\text{aq})}$   $(2 \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{O}_{2(\text{g})} + 4 \text{H}^{+}_{(\text{aq})} + 4 \text{e}^{-})$

Reaction:  $2 \text{H}_2\text{O}_{(\text{l})} \rightarrow 2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$

**Q4:** What are the products of the electrolysis of  $\text{AgNO}_{3(\text{aq})}$ ?

**A4:** at the cathode:  $\text{Ag}_{(\text{s})}$   $(\text{Ag}^{1+}_{(\text{aq})} + \text{e}^{-} \rightarrow \text{Ag}_{(\text{s})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}^{1+}_{(\text{aq})}$   $(2 \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})} + 4 \text{e}^{-})$

Reaction:  $4 \text{Ag}^{1+}_{(\text{aq})} + 2 \text{H}_2\text{O}_{(\text{l})} \rightarrow 4 \text{Ag}_{(\text{s})} + \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})}$

**Q5:** What are the products of the electrolysis of aqueous  $\text{Al}(\text{NO}_3)_3$ ?

**A5:** at the cathode:  $\text{H}_{2(\text{g})}$  &  $\text{OH}^{1-}_{(\text{aq})}$        $(2 \text{H}_2\text{O}_{(\ell)} + 2 \text{e}^{1-} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{1-}_{(\text{aq})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}^{1+}_{(\text{aq})}$        $(2 \text{H}_2\text{O}_{(\ell)} \rightarrow \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})} + 4 \text{e}^{1-})$

Reaction:  $2 \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$

**Q6:** What are the products of the electrolysis of aqueous  $\text{HNO}_3$ ?

**A6:** at the cathode:  $\text{H}_{2(\text{g})}$        $(2 \text{H}^{1+}_{(\text{aq})} + 2 \text{e}^{1-} \rightarrow \text{H}_{2(\text{g})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}^{1+}_{(\text{aq})}$        $(2 \text{H}_2\text{O}_{(\ell)} \rightarrow \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})} + 4 \text{e}^{1-})$

Reaction:  $2 \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$

**Q7:** What are the products of the electrolysis of aqueous  $\text{CuSO}_4$ ?

**A7:** at the cathode:  $\text{Cu}_{(\text{s})}$        $(\text{Cu}^{2+}_{(\text{aq})} + 2 \text{e}^{1-} \rightarrow \text{Cu}_{(\text{s})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}^{1+}_{(\text{aq})}$        $(2 \text{H}_2\text{O}_{(\ell)} \rightarrow \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})} + 4 \text{e}^{1-})$

Reaction:  $2 \text{Cu}^{2+}_{(\text{aq})} + 2 \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{Cu}_{(\text{s})} + \text{O}_{2(\text{g})} + 4 \text{H}^{1+}_{(\text{aq})}$

**Q8:** What are the products of the electrolysis of aqueous  $\text{KOH}$ ?

**A8:** at the cathode:  $\text{H}_{2(\text{g})}$  &  $\text{OH}^{1-}_{(\text{aq})}$        $(2 \text{H}_2\text{O}_{(\ell)} + 2 \text{e}^{1-} \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}^{1-}_{(\text{aq})})$

at the anode:  $\text{O}_{2(\text{g})}$  &  $\text{H}_2\text{O}_{(\ell)}$        $(4 \text{OH}^{1-}_{(\text{aq})} \rightarrow \text{O}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\ell)} + 4 \text{e}^{1-})$

Reaction:  $2 \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$

# Chapter-20

## Lesson-9

### IX – Quantitative Aspects of Electrochemistry

#### A) Electrolytic Stoichiometry

- The **coulomb** (C) is the SI unit of electric charge.  
One electron has a charge of  $1.602 \times 10^{-19}$  C.  
One mole of electrons has a charge of 96485 C.  
One coulomb (1 C) is equal to the charge of  $6.242 \times 10^{18}$  e<sup>-</sup>.  
One coulomb (1 C) is equal to one ampere•second (1 A•s)

$$q = I \times t \quad (q \text{ is the variable for Coulombs})$$

- The **ampere** (A) is the SI unit for current. (1 A = 1 C per second)

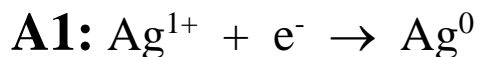
$$I = q/t \quad (I \text{ is the variable for Amperes})$$

- The **volt** (V) is the unit of electric potential. (1 V = 1 Joules per C)

$$V = E/q \quad (V \text{ is the variable for Volts})$$

- 96485 C per mole of electrons is called **Faraday's constant** (F )
- 1 F (1 Faraday) = 96485 C = 1 mole e<sup>-</sup> = 96485 A•s

**Q1:** How many grams of silver is plated from a AgNO<sub>3</sub> solution by a 9.00 V battery that uses 84200 J of energy?



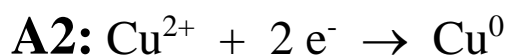
$$V = E/q$$

$$9.00 = 84200/q$$

$$q = 9360 \text{ C}$$

$$9360 \text{ C} \times \frac{1 \text{ mol e}^{-}}{96485 \text{ C}} \times \frac{1 \text{ mol Ag}^0}{1 \text{ mol e}^{-}} \times \frac{107.9 \text{ g Ag}^0}{1 \text{ mol Ag}^0} = \boxed{10.5 \text{ g Ag}^0}$$

**Q2:** How much time is required to produce 1.00 g of copper metal from a  $\text{CuSO}_4$  solution with 10.0 amperes.



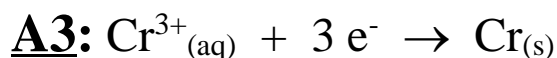
$$1.00 \text{ g Cu}^0 \times \frac{1 \text{ mol Cu}^0}{63.6 \text{ g Cu}^0} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}^0} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} = 3030 \text{ C}$$

$$I = q/t$$

$$10.0 = 3030/t$$

$$t = 303 \text{ s or } 5 \text{ min } 3 \text{ s}$$

**Q3:** A faucet is being plated with 0.86 g of  $\text{Cr}_{(\text{s})}$  from an electrolytic bath containing aqueous  $\text{Cr}_2(\text{SO}_4)_3$ . If 12.5 min. is allowed for plating, then how much current is needed

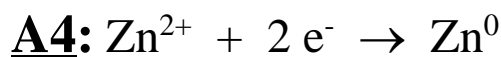


$$0.86 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96485 \text{ C}}{1 \text{ mol e}^-} = 4800 \text{ C}$$

$$I = q/t$$

$$I = \frac{4800 \text{ C}}{12.5 \text{ min}} \times \frac{1 \text{ min}}{60.0 \text{ s}} = 6.4 \text{ A}$$

**Q4:** Zinc plating (galvanizing) is usually done by dipping the object into molten zinc. However zinc can also be electroplated from aqueous zinc solutions. How many grams of zinc can be plated on a steel tank from a  $\text{ZnSO}_4$  solution when a 0.755 A current is applied for 2.00 days?



$$q = I \times t$$

$$q = 0.755 \times 172800 = 130464 \text{ C}$$

$$130464 \text{ C} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Zn}}{2 \text{ mol e}^-} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 44.21 \text{ g Zn}$$

## B) Electrical Work

- A **watt** (W) is a unit of power (P).  
1 **watt** (W) is equal to 1 joule per second (1 J/s).  $P = E \div t$   
1 **watt** (W) is equal to 1 volt•ampere (1 V•A).  $P = V \times I$
- A **kilowatt** (1 kW) is equal to 1000 W or 1000 J/s or to 1000 V•A
- A **kilowatt-hour** (1 kW•h) is equal to  $3.6 \times 10^6$  J (**exact quantity**)  
 $1 \text{ kW}\cdot\text{h} = 1000 \text{ W} \cdot 3600 \text{ s} = 1000 \text{ J/s} \cdot 3600 \text{ s} = 3.6 \times 10^6 \text{ J}$  ( $\infty$  sig figs)
- **Electrical work** is often measured in kilowatt-hours.
- The maximum amount of electrical work produced by the redox reaction in a voltaic cell is ...

$$w_{\max} = \Delta G = -nFE_{\text{cell}}$$

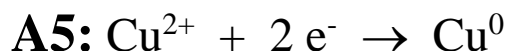
where E is the **emf** of the cell.

- The amount of electrical work done on the redox reaction in electrolysis is ...

$$w = nFE_{\text{ext}}$$

where  $E_{\text{ext}}$  is the applied external potential.

**Q5:** Like any piece of apparatus, an electrolytic cell operates at less than 100% efficiency. A cell that deposits Cu from a  $\text{Cu}^{2+}$  bath operates for 10 h with an average current of 5.8 A. If 53.4 g of copper is deposited, at what efficiency is the cell operating?



$$q = I \times t$$

$$q = 5.8 \times 36000 = 208800 \text{ C}$$

$$208800 \text{ C} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Cu}^0}{2 \text{ mol e}^-} \times \frac{63.6 \text{ g Cu}^0}{1 \text{ mol Cu}^0} = 68.8 \text{ g Cu}^0$$

$$\% \text{ efficiency} = \frac{53.4 \text{ g}}{68.8 \text{ g}} \times 100 = \boxed{77.6 \%}$$

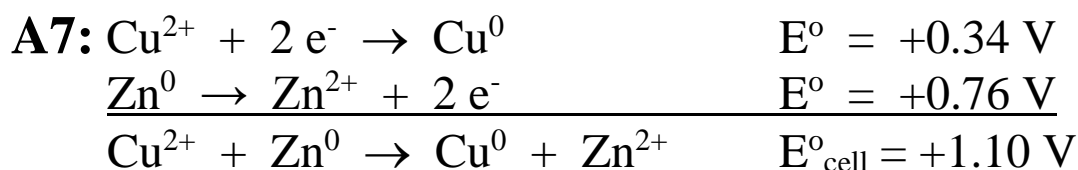
**Q6:** An electric kettle heats 2.00 L of water from 20.0°C to 100.0°C in 5.00 min. If the supply voltage is 200.0 V, then calculate the energy consumed in kW•h.

**A6:**  $q = mc\Delta T = (2000)(4.18)(80.0) = 669000 \text{ J}$

$$669000 \text{ J} \times 1 \text{ kW}\cdot\text{h}/3600000 \text{ J} = \boxed{0.185 \text{ kW}\cdot\text{h}} \quad \text{OR}$$

$$P = \frac{q}{t} = \frac{669000 \text{ J}}{300 \text{ s}} = 2230 \text{ W} \rightarrow 2.23 \text{ kW} \times \frac{1 \text{ h}}{12} = \boxed{0.185 \text{ kW}\cdot\text{h}}$$

**Q7:** Consider the voltaic cell:  $\text{Zn}_{(\text{s})}/\text{Zn}^{2+}_{(\text{aq})} \parallel \text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$ . Under standard conditions, what is the maximum amount of work, *in joules*, that the cell can accomplish if 50.0 g of Cu is produced?



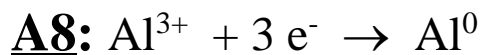
$$w_{\text{max}} = \Delta G = -n\mathcal{F}E^{\circ} = -(2)(96485)(+1.10) = -212000 \text{ J/mol}$$

$$50.0 \text{ g Cu}^0 \times \frac{1 \text{ mol Cu}^0}{63.6 \text{ g Cu}^0} \times \frac{-212000 \text{ J}}{1 \text{ mol Cu}^0} = \boxed{-167000 \text{ J}}$$

**Q8:** Al metal is produced from the electrolysis of  $\text{Al}_2\text{O}_3$  using 6.00 V.

(i) How much energy (J) is needed to produce 1.00 kg Al?

(ii) What is the cost (in \$) at the rate of **16.1 ¢** per 1 kW•h?



$$(i) 1000 \text{ g Al}^0 \times \frac{1 \text{ mol Al}^0}{26.98 \text{ g}} \times \frac{3 \text{ mole e}^{-}}{1 \text{ mole Al}^0} \times \frac{96485 \text{ C}}{1 \text{ mol e}^{-}} = 1.07 \times 10^7 \text{ C}$$

If  $V = E/q$ , then  $E = V \times q$

$$6.00 \text{ V(J/C)} \times 1.07 \times 10^7 \text{ C} = \boxed{6.42 \times 10^7 \text{ J}}$$

$$(ii) 6.42 \times 10^7 \text{ J} \times \frac{1 \text{ kW}\cdot\text{h}}{3.6 \times 10^6 \text{ J}} \times \frac{\$0.16}{\text{ kW}\cdot\text{h}} = \boxed{\$ 2.85}$$